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Reactivity Ratios of Isobutyl POSS-Styrene and Styrene Monomers

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Introduction

Copolymers containing POSS (Polyhedral Oligomeric Silsesquioxane) generally have higher mechanical and thermal properties than polymers without POSS.

The microstructure that leads to these increases may be caused by POSS nanoparticle units or aggregates of these units to form larger POSS clusters.

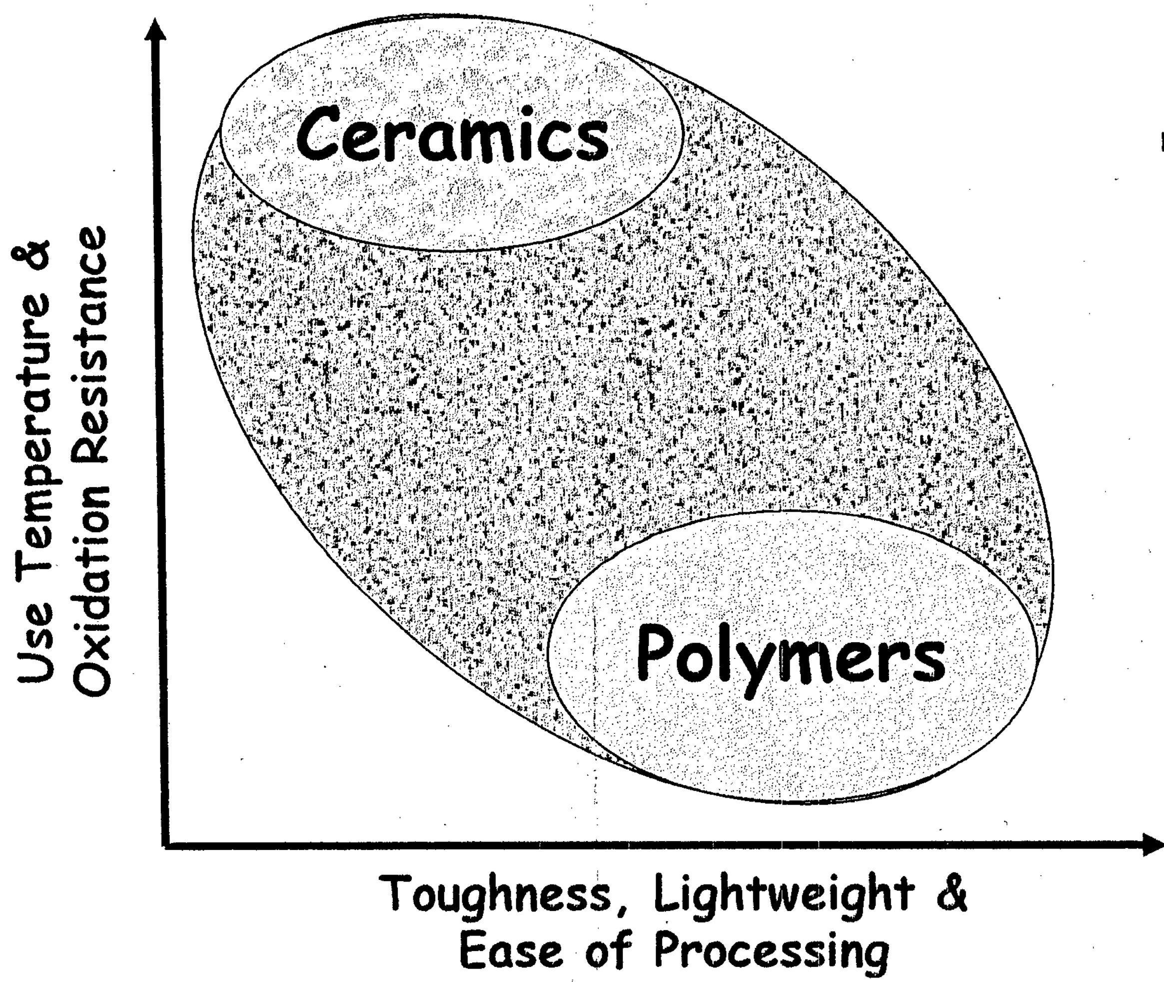
To help define the microstructure of the addition copolymers, the POSS macromer and organic monomer reactivity ratios (r_1 and r_2) need to be known.

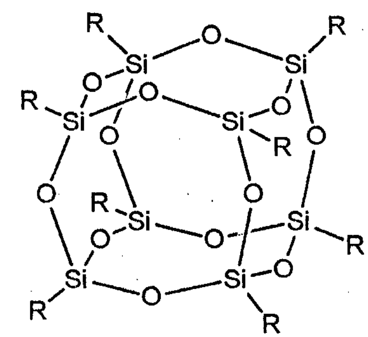
Alternating Copolymerization: $r_1 = r_2 = 0$

Block Copolymerization: $r_1 > 1$, $r_2 > 1$

Random Copolymerization: $r_1 r_2 = 1$

Hybrid Inorganic/Organic Polymers

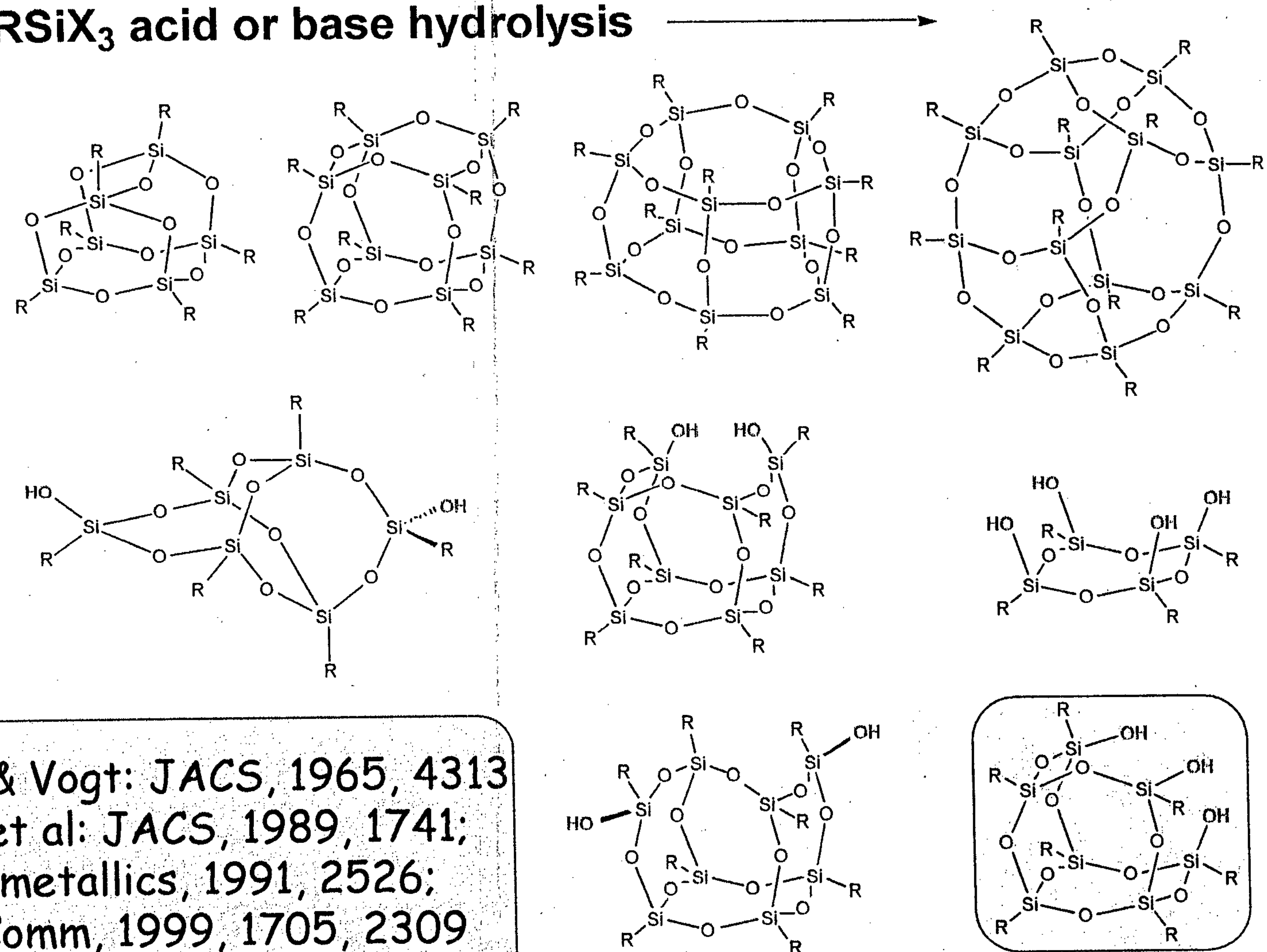




Hybrid plastics bridge the differences between ceramics and polymers.

POSS Synthesis

$RSiX_3$ acid or base hydrolysis →



Brown & Vogt: JACS, 1965, 4313
Feher et al: JACS, 1989, 1741;
Organometallics, 1991, 2526;
Chem Comm, 1999, 1705, 2309

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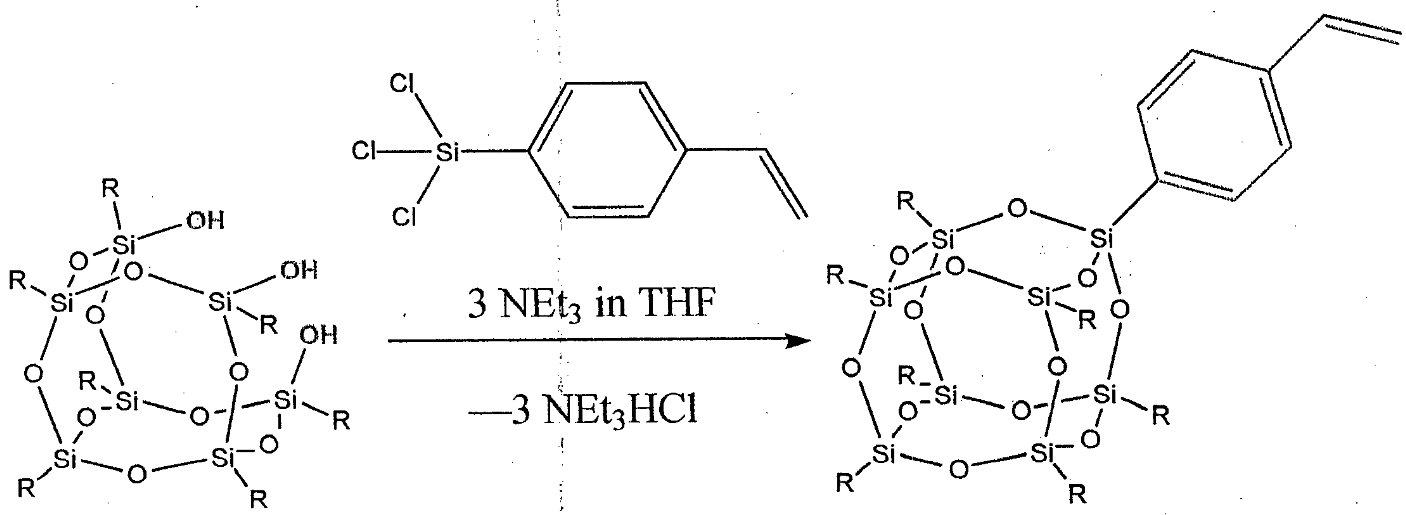
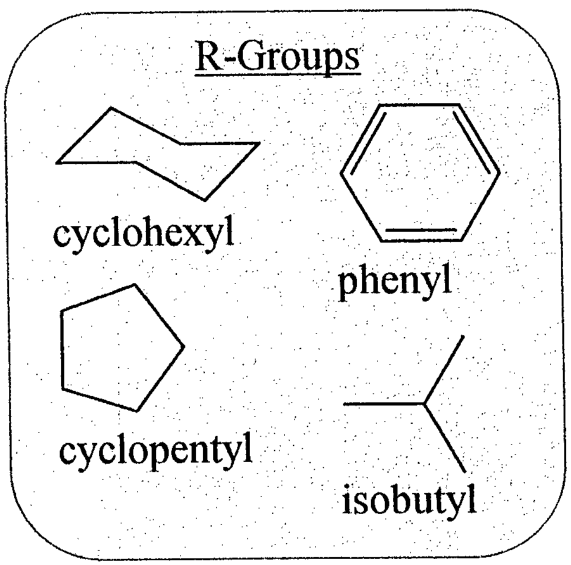
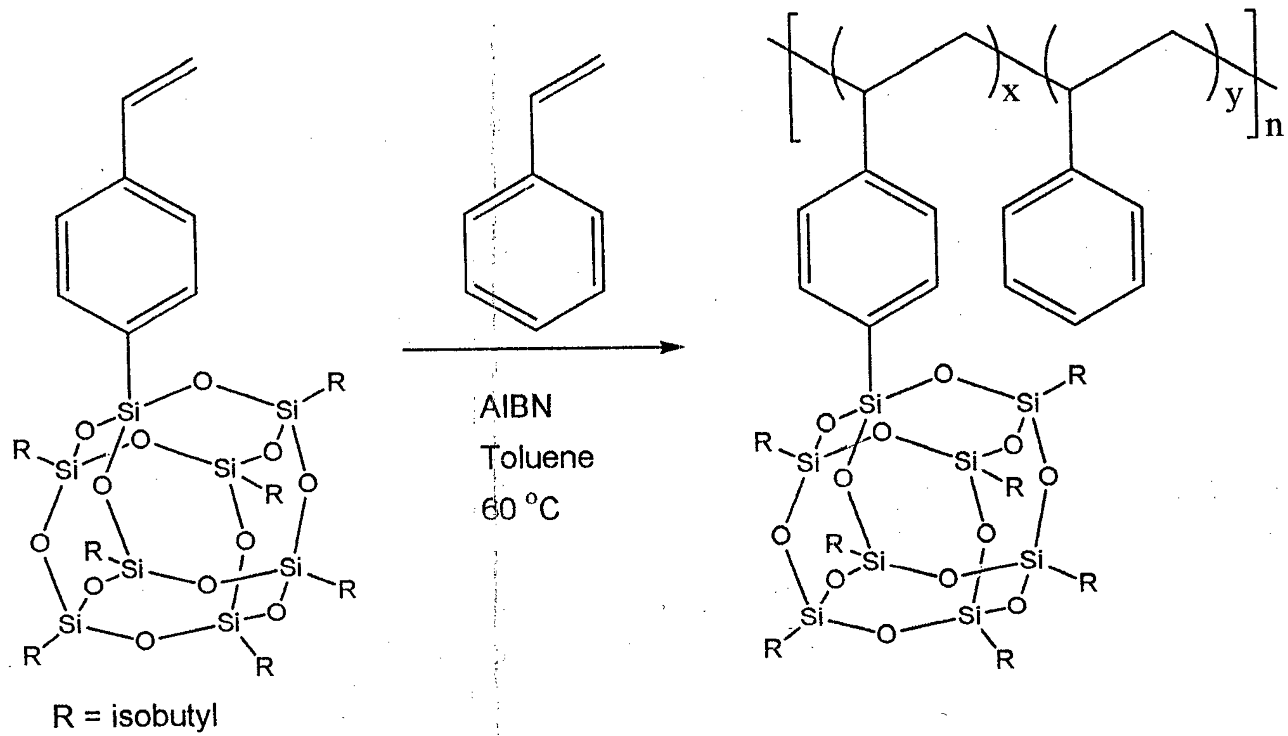
POSS-Styrene Monomer Synthesis





- High-yield syntheses.
- Phenyl derivative requires inverse addition.
- J. Inorg. Organomet. Polym., Vol 11, 2002, p. 155.

POSS-Styrene Copolymer Synthesis



- Solution polymerization in toluene or bulk polymerization possible.
- Polymerization is limited by solubility of the POSS-macromer.
- Isobutyl-POSS is the most soluble, Phenyl-POSS the least soluble.
- Macromolecules Vol. 29, 1996 p. 7302.

Reactivity Ratios for Styrene / POSS-Styrene

M_1: Styrene Monomer

M_2: POSS-Styrene Monomer

M_1^*: growing polymer M_1-radical

M_2^*: growing polymer M_2-radical

r_1: reactivity ratio for Styrene

r_2: reactivity ratio for POSS-Styrene

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$$
$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$$
$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$$
$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$$

$$r_1 = \frac{k_{11}}{k_{12}}$$
$$r_2 = \frac{k_{22}}{k_{21}}$$

The composition of a copolymer cannot be determined by the homopolymerization rates of the two monomers.

Assume the chemical reactivity of the propagating chain in a copolymerization to be dependent on the monomer at the growing end.

Reactivity Ratios for Styrene / POSS-Styrene

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Alternating Copolymerization: $r_1 = r_2 = 0$

Block Copolymerization: $r_1 > 1$, $r_2 > 1$

Random Copolymerization: $r_1 r_2 = 1$

Reactivity Ratios calculated using the copolymer composition equation:

$$F_1 = \frac{(r_1 f_1 f_1 + f_1 f_2)}{(r_1 f_1 f_1 + 2 f_1 f_2 + r_2 f_2 f_2)}$$

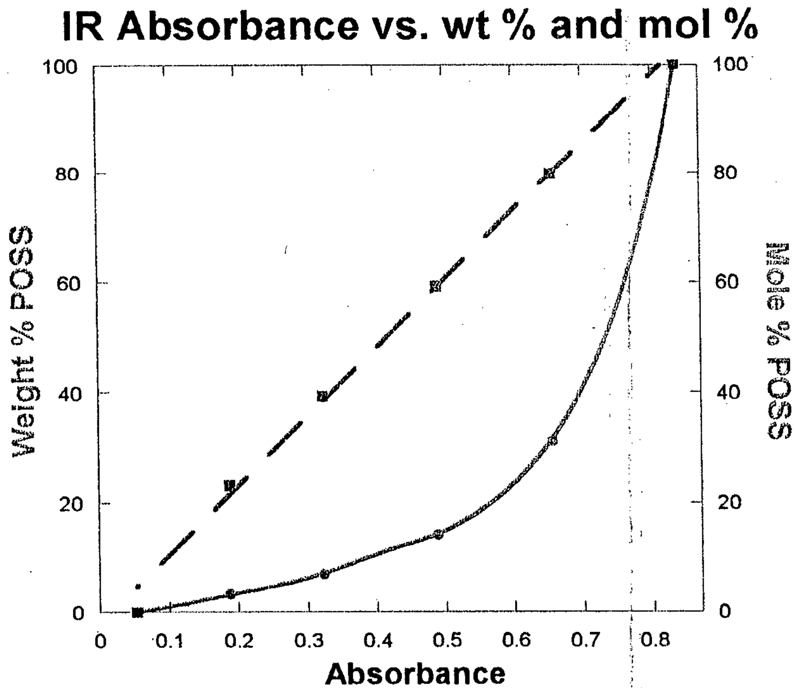
r_1 = reactivity ratio for styrene
r_2 = reactivity ratio for POSS-styrene
F_1 = mole fraction of styrene in copolymer
f_1 = mole fraction of styrene monomer in feed
f_2 = mole fraction of POSS monomer in feed

Reactivity Ratios: Challenges

- Polymerizations <u>must</u> be carried out to only 3-5% completion.
  -Reactions were run for 3 hours and monitored by ^{1}H NMR.
- The small amount of polymer formed (a solid) must be separated from unreacted POSS-monomer (also a solid).
  -Achieved with precipitation of copolymer using Chloroform/MeOH
- Carry out a full (10-90) range of mole % POSS reactions while maintaining the same concentration of monomers and initiator.
  -Achieved best with isoButylPOSS as it has favorable solubility.
- Accurately determine the amount of POSS in each copolymer.
  -NMR integration is more accurate than IR analysis over the full mole % range.

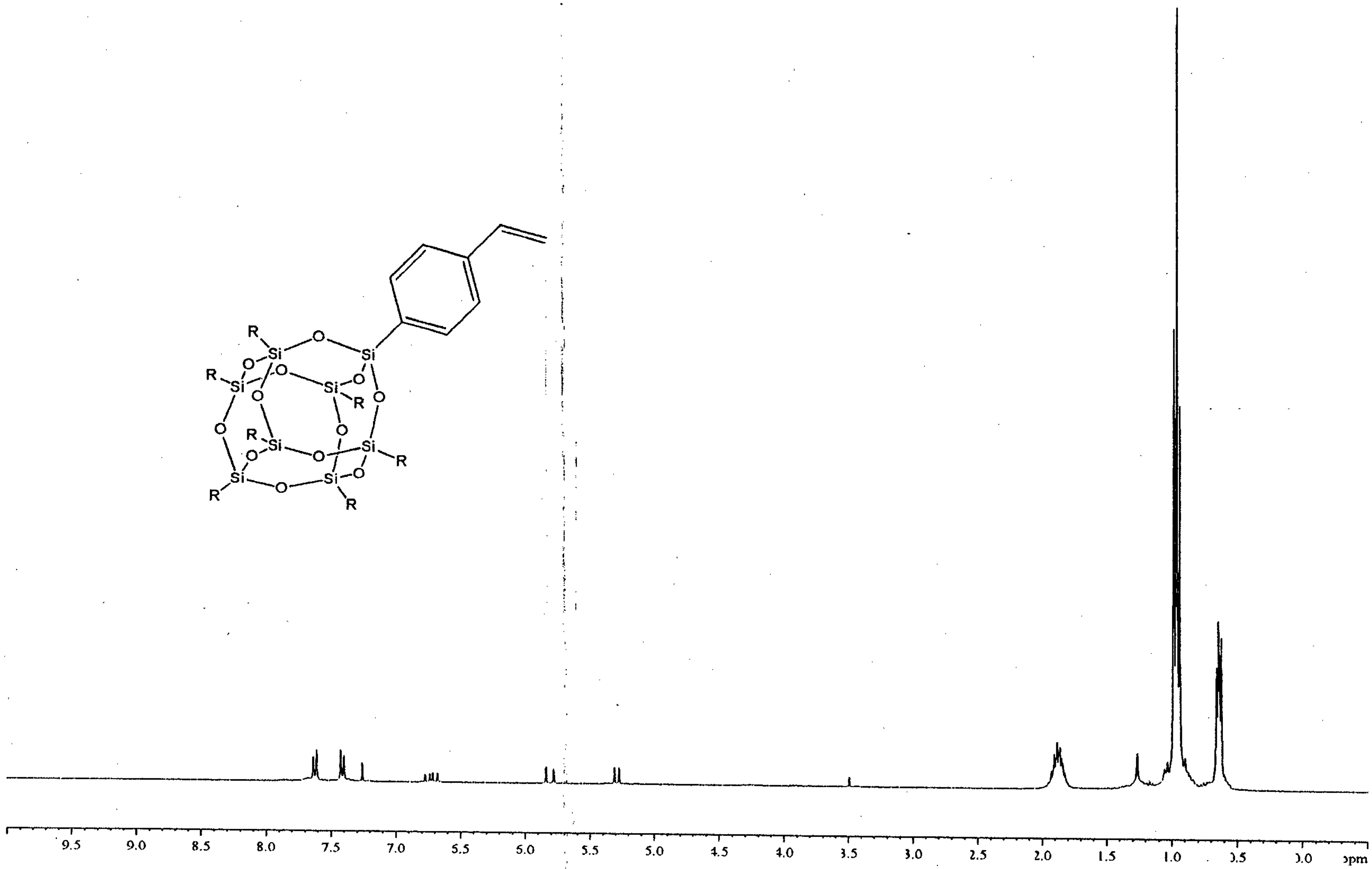
Compositional Analysis with FTIR

FTIR can be used to determine weight % POSS in a copolymer as there is a linear response between weight % POSS and absorbance. However, because a POSS is a such a large macromer, there is <u>NOT</u> a linear response using mole % POSS (see graph below).



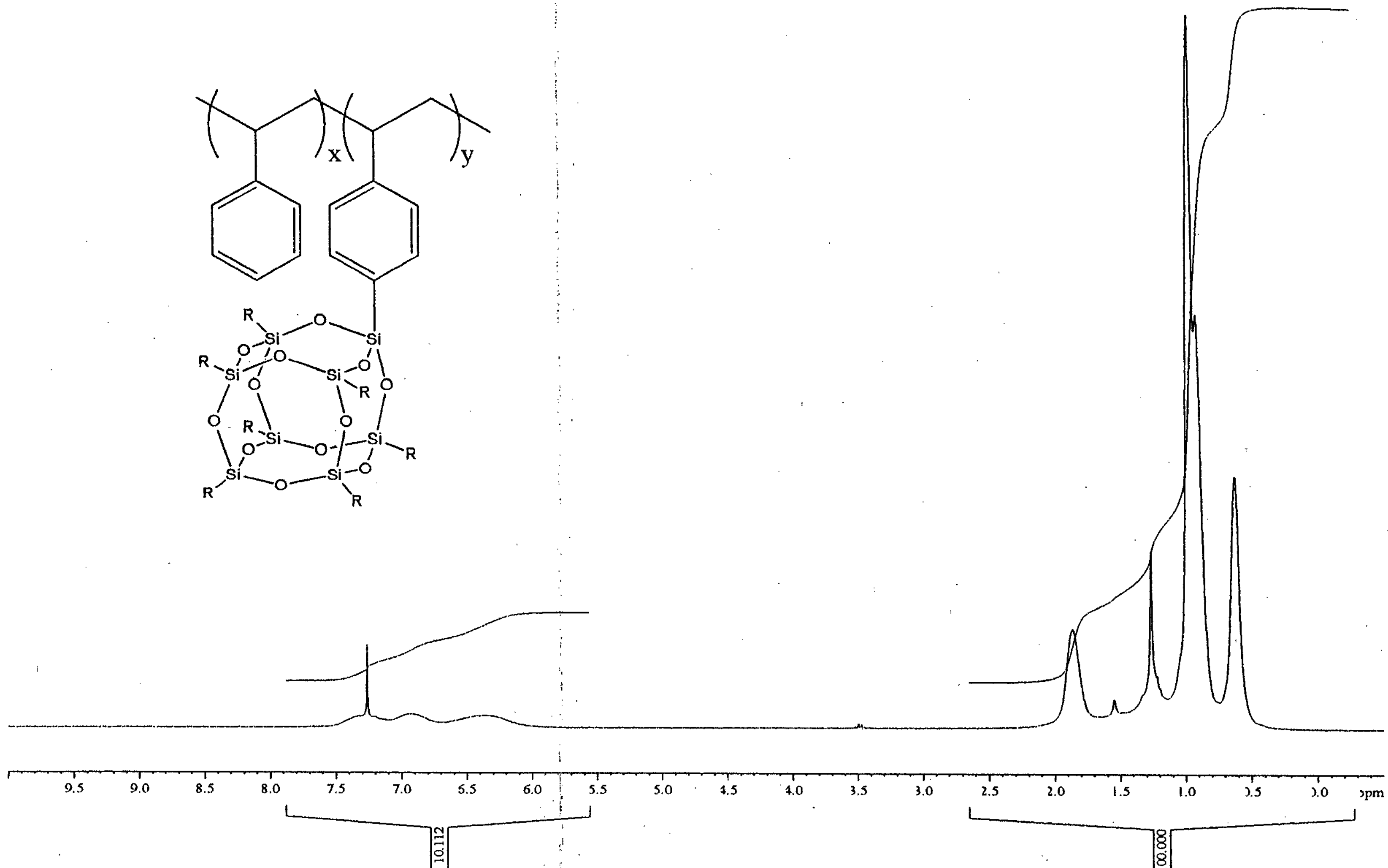
Note that IR analysis is an excellent method for determining mole % POSS in the low to 25 mole % POSS range

^1H NMR Spectrum of Crude Reaction Solids



This spectrum shows mostly POSS-monomer with some copolymer.

^1H NMR Spectrum of Isolated Copolymer



This spectrum shows monomer-free copolymer.

Copolymer Composition

Composition determined from 2 equations and 2 unknowns using ^1H NMR

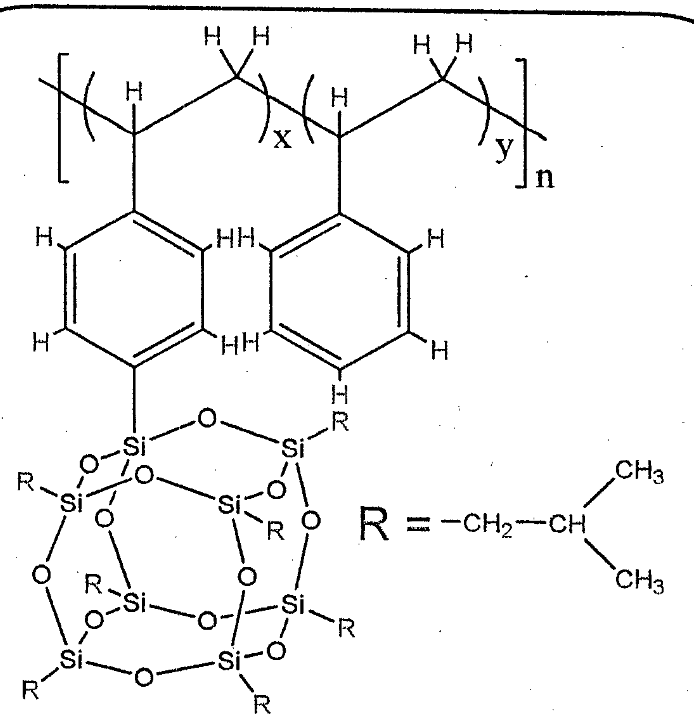
x = mole fraction POSS-styrene
y = mole fraction styrene

$$x + y = 1 \qquad \boxed{y = 1 - x} \qquad (1)$$

$$\text{Integral Ratio (IR)} = \frac{\text{Aromatic Integral}}{\text{Aliphatic Integral}} = \frac{4x + 5y}{66x + 3y} \qquad (2)$$

Solving for x:

$$x = \frac{5 - 3IR}{63IR + 1}$$



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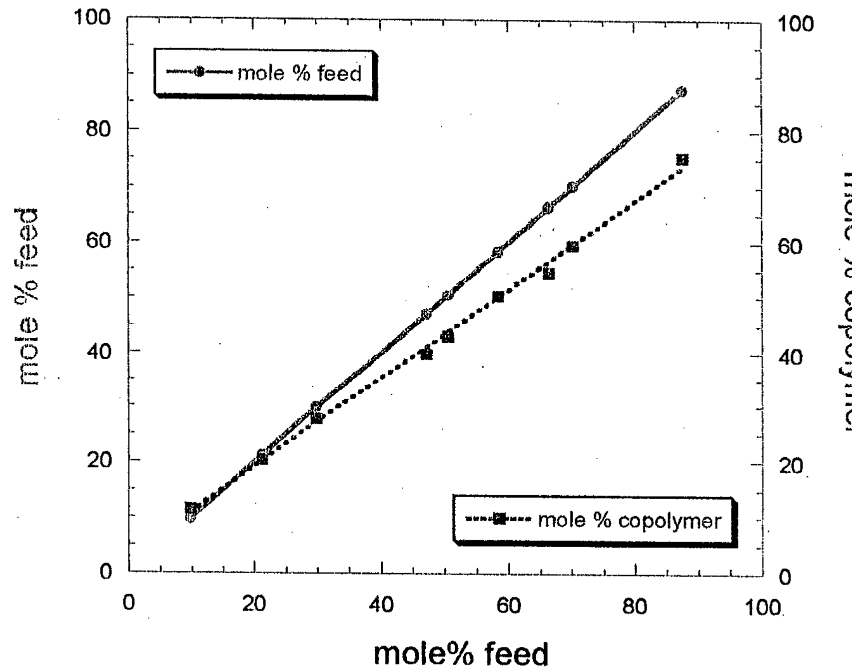
Experimental Data

Experiment #	POSS in Feed		POSS in Copolymer	
	weight %	mole %	weight %	mole %
1	48.91	9.78	53.60	11.57
2	70.42	21.24	69.33	20.38
3	78.98	29.85	77.19	27.71
4	88.73	47.14	85.39	39.83
5	90.01	50.50	86.98	43.07
6	92.53	58.38	89.97	50.39
7	94.58	66.40	91.40	54.62
8	95.42	70.24	92.85	59.53
9	98.42	87.57	96.43	75.38

Mole % Feed vs. Mole % Copolymer



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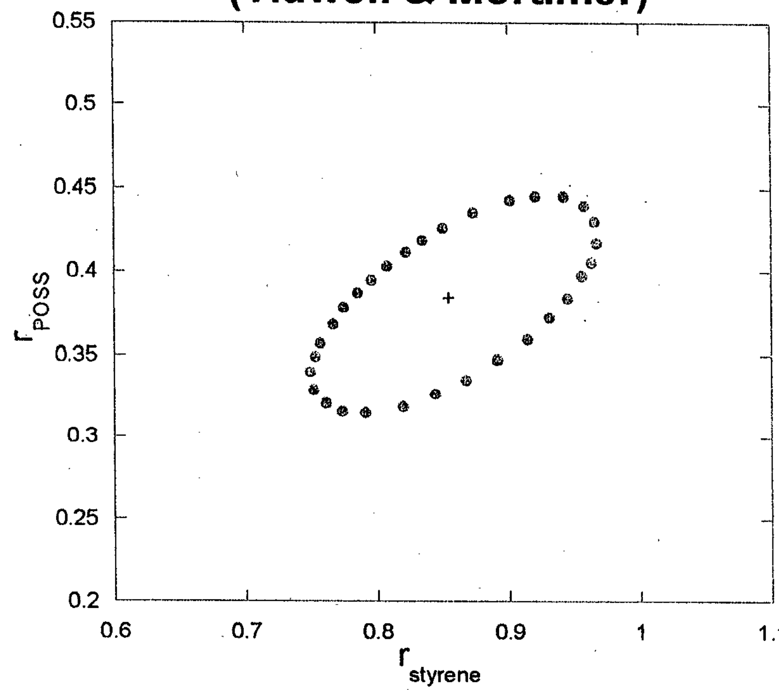
Determination of Reactivity Ratios

Method	Reactivity Ratios	
	$r_{styrene}$	r_{POSS}
Fineman-Ross	0.77	0.34
Kelen-Tudos	0.82	0.37
Yezrielev-Brokhina-Roskin	0.79	0.35
Tidwell-Mortimer	0.84	0.38

95% Confidence Interval (Tidwell & Mortimer)



Tidwell-Mortimer is a nonlinear least squares method.

Calculations and Confidence Interval were obtained using a program supplied in the book "Copolymerization Toward a Systematic Approach" by Cornel Hagiopol.

Summary and Future Work

- $r_{styrene} = 0.84$ and $r_{POSS} = 0.38$, therefore a copolymer sequence should be close to random.
- Copolymer compositions are best analyzed using NMR and not FTIR spectroscopy because copolymerizations are done over a full 10 to 90 mole % POSS. FTIR analysis is accurate up to approximately 25 mole % POSS incorporation.
- Q and e values (polarity and reactivity) for i-butyl POSS styrene will be determined after reactivity ratios with methacrylate and acrylonitrile are completed.

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